

## Synthesis and Structural Characterization of Polypyrrole/Metal Oxide Composite by NMR Spectroscopy

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### ABSTRACT

The structure of Polypyrrole (PPy) has been widely studied by using various spectroscopic techniques which indicates that all nitrogen atoms of Polypyrrole (PPy) are protonated resulting in chain the of linked pyrrole molecules, and made ease to oxidative polymerization of pyrrole. For characterizing structure of such conducting polymers in the solution and in solid state high resolution NMR Spectroscopic techniques have developed the most powerful tool. Some PPy / Metal Oxide composite were prepared by chemical oxidation polymerization in non-aqueous medium and characterized by NMR technique.

**Keywords:** Polypyrrole (PPy); Conducting Polymer; NMR; oxidative polymerization.

### INTRODUCTION

As a advanced material, intrinsic conducting polymers with p-conjugated double bonds and imines nitrogen have been attracted much attention in recent years. Among all these conducting polymers , Polypyrrole (PPy) and its structure were attracted considerable interests because of

its good environmental stability, facile synthesis, and higher conductivity and promising commercial applications than many other conducting polymers.

But, unfortunately the fact is that PPy is insoluble makes the elucidation of molecular structure more difficult. Generally, structural problem of PPy in solid state<sup>1</sup> can conveniently studied by using

High resolution NMR Spectroscopic techniques.<sup>2-4</sup> High resolution NMR Spectroscopic techniques have developed the most powerful method available for characterizing structure of conducting polymers in the solution and in solid state.

The chemical shift<sup>5</sup>, spin-spin interaction, coupling constant are one of the most important parameter used for structural elucidation of polymers. The NMR chemical shift provides details information of the structure, non-crystalline, and crystalline nature. Some PPy/Metal Oxide composite was prepared by chemical oxidation polymerization in non-aqueous medium of diethyl ether. Anhydrous FeCl<sub>3</sub> was used as oxidant. All results depended on the FeCl<sub>3</sub>/pyrrole feed composition. The product was analyzed by NMR Spectroscopic techniques.

## 2. EXPERIMENTAL

### 2.1 Reagents and Raw Materials

Pyrrole (AR Grade –Aldrich, India) monomer was distilled under reduced pressure, put in a desiccators and stored in the refrigerator to use. Ethyl Ether (AR grade, S.D. Fine Chemicals, India) was used as solvent, and anhydrous FeCl<sub>3</sub> (Laboratory grade) as oxidant. Ethanol, acetone, ZnO, PbO, MnO<sub>2</sub>, (AR grade, S.D. Fine Chemicals, India) were other analytical reagents and were used as received. Double distilled water was used for the preparation of all the solutions.

### 2.2 Sample Preparation<sup>6</sup>

Ethyl Ether 50 ml was added to a specific amount of anhydrous FeCl<sub>3</sub> in 100 ml round bottom flask with continuous

stirring with a magnetic stir bar, and then 1g of distilled pyrrole and 1g PbO/ZnO/MnO<sub>2</sub> were added to the stirred solution at 0°C. After a reaction time of 1.5 hrs, the black precipitate was obtained as a composite material. The product was washed by water, followed by ethanol and dried which was named as PPY- FeCl<sub>3</sub> / PPY – PbO / PPY – ZnO / PPY – MnO<sub>2</sub> respectively.

## 3. RESULT AND DISCUSSION

### 3.1 Solubility

Solubility of PPy-FeCl<sub>3</sub>, PPy-ZnO, PPy-PbO, and PPy-MnO<sub>2</sub> composite was tested in many organic solvents at room temperature. It is summarized in Table 1 and 2. It has been seen that almost all the polymers are partially soluble only in strong hydrogen bonding solvents like DMF, DMSO and are insoluble in common organic solvents like alcohol, benzene, etc.

**Table 1 : Solubility of Polymer in Strong Hydrogen bonding Solvents**

S. No.	Polymers	Solvents	Solubility
1	PPY - FeCl <sub>3</sub>	DMF, DMSO	Partially Soluble
2	PPY - ZnO	DMF, DMSO	Partially Soluble
3	PPY - PbO	DMF, DMSO	Partially Soluble
4	PPY –MnO <sub>2</sub>	DMF, DMSO	Partially Soluble

**Table 2 : Solubility of Polymer in Common Organic Solvents**

S. No.	Polymers	Solvents	Solubility
1	PPY - FeCl <sub>3</sub>	Ethyl alcohol / Benzene	Insoluble
2	PPY - ZnO	Ethyl alcohol / Benzene	Insoluble
3	PPY - PbO	Ethyl alcohol / Benzene	Insoluble
4	PPY –MnO <sub>2</sub>	Ethyl alcohol / Benzene	Insoluble

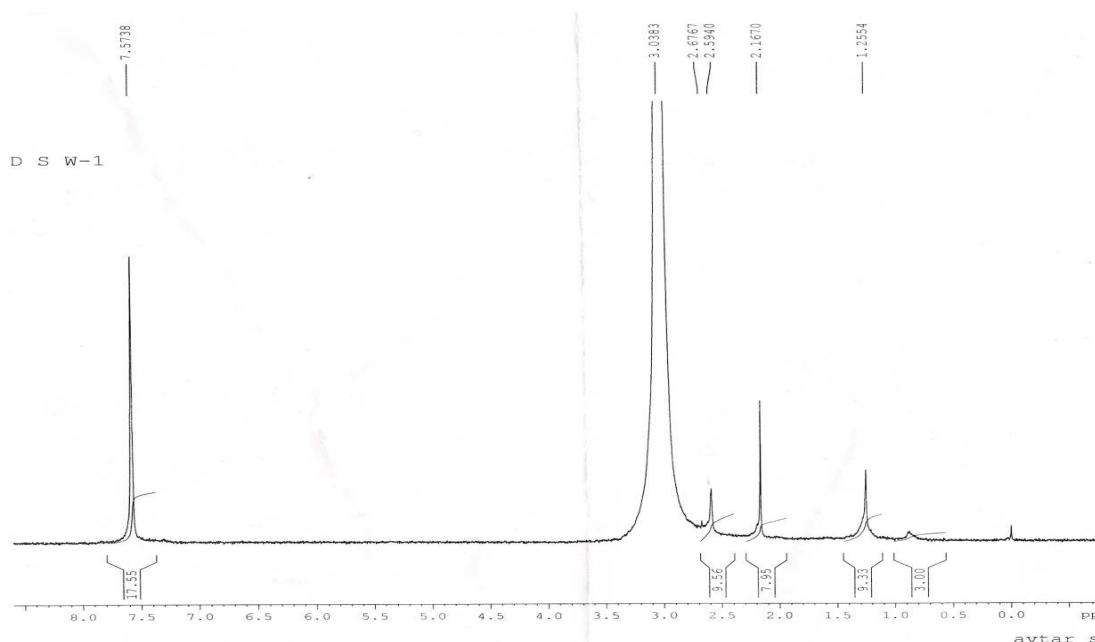
### 3.2 Melting temperatures of Polymers

Generally, when polymer melts, the low molecular weight part of it melts first while the high molecular weight part of it melts later. Due to this there is no sharp melting point as such but a range of temperature. The melting range (i.e. the temperature at which the samples starts phase separation and the temperature at which melting completes with no solid phase) of polymer has to be noted instead of melting point. Table 3 gives the melting

point of the polymers. All the polymer samples shows the melting point above 350<sup>0</sup>C that means all the polymer samples are thermally stable due to the crystalline nature of the macromolecules.

**Table 3 : The Melting point of the Polymer**

S. No.	Polymers	Melting Point
1	PPy – FeCl <sub>3</sub>	Above 350 <sup>0</sup> C
2	PPy – ZnO	Above 350 <sup>0</sup> C
3	PPy – PbO	Above 350 <sup>0</sup> C
4	PPy – MnO <sub>2</sub>	Above 350 <sup>0</sup> C



**Fig. 1 : NMR Spectra of PPy - FeCl<sub>3</sub>**

### 3.3 Nuclear Magnetic Resonance

For proton magnetic resonance studies of non aqueous solution the most recommended reference compound is tetra methyl silane (TMS), which is magnetically and electrically isotropic, chemically

reasonably inert, and non-associating with any common compound. When the high field absorbing tetra methyl silane used as a reference, most delta values are negative. The chemical shifts are solvents dependent.

The spin-spin interactions occur mostly between nuclei which are one to four

bonds away from each other in the molecule. These spin-spin interactions called coupling constants can be approximately determined even in very complex spectra, coupling constant, e.g. between the two protons or C-13 nucleus and a proton are molecular parameters, independent of the applied external magnetic field, express is hertz; they can have positive or negative values depending on the number of bonds between the two nuclei.

As the coupling constants, especi-

ally between the two protons on the adjacent carbon atoms, are very sensitive to the rotational changes, one can also derive from them the preferred conformation of the polymer chain.<sup>7-8</sup> From <sup>1</sup>H NMR spectra of the samples shows that in polymerization the linkage between two monomer of pyrrole is  $\alpha, \alpha'$  in the polymer chain. NMR values for polypyrrole are  $\delta$  at .0.8743, 1.1424, 0.8743, 0.8743 gives N-H peaks while  $\delta$  at 1.25, 1.2511, 1.2502, 1.2554 gives pyrrole peak.

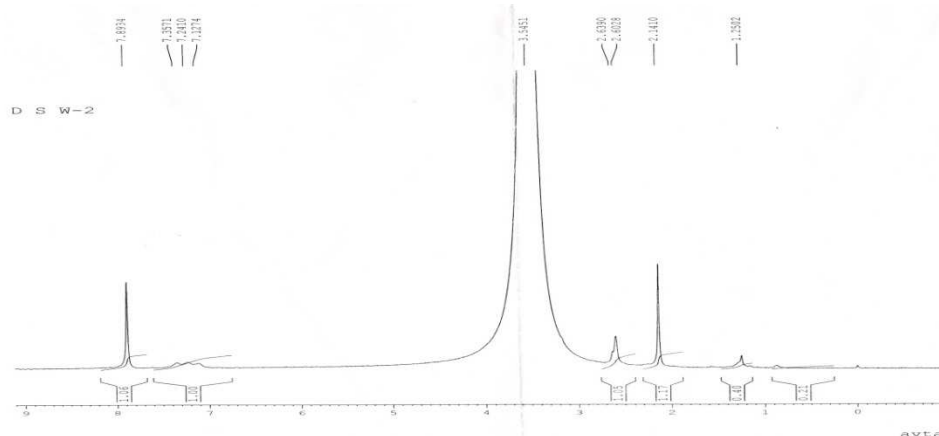


Fig.2 : NMR Spectra of PPy – ZnO

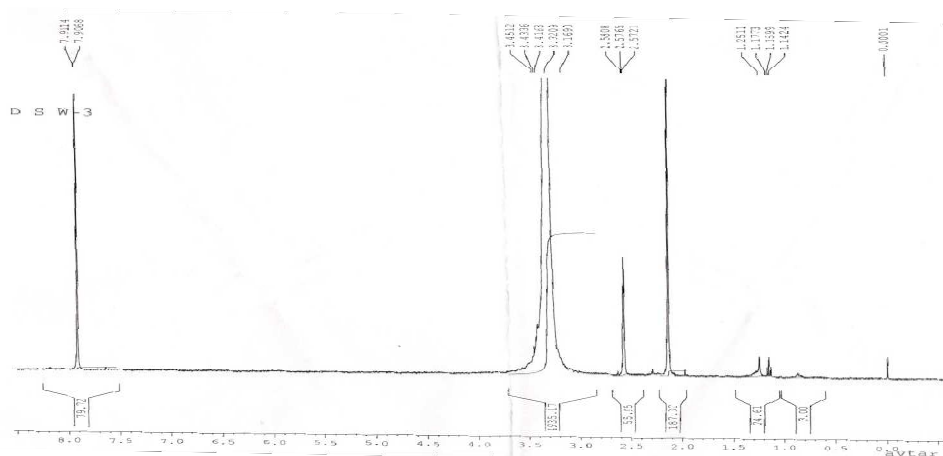


Fig. 3 : NMR Spectra of PPy- PbO<sub>2</sub>

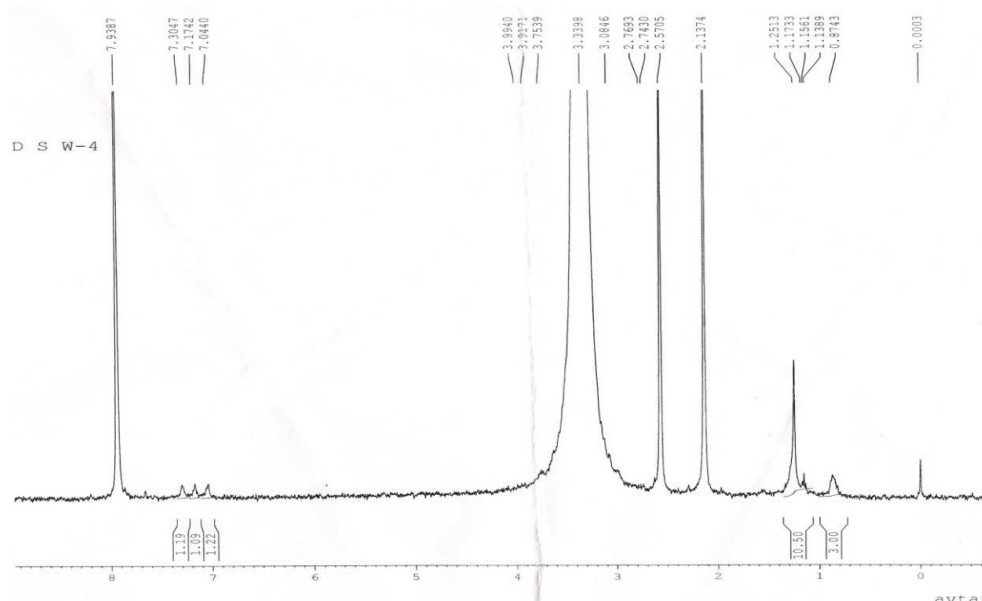


Fig. 4 : NMR Spectra of PPy - MnO<sub>2</sub>

## CONCLUSION

Polypyrrole with transition metal salt composite polymer has been prepared by using oxidation polymerization. The samples have been characterized by NMR spectroscopic methods. Melting temperature of polypyrrole with transition metal salt composite polymer is recorded above 350<sup>0</sup> C. It is concluded that these composite polymers are thermally stable.

NMR spectra confirmed the polymeric linkage and also the attachment of the salts. Nitrogen atoms bounded to a hydrogen atom can be observed. In pyrrole ring nitrogen atoms remains protonated. The chemical shift of pyrrole ring atom experience a small high-field shift<sup>9</sup>. The observation of dominant in homogeneous line broadening indicates from all ideal arrangement of polypyrrole<sup>10</sup> which assumes that the pyrrole ring of a given

chain linked in  $\alpha$ -position and arranged in a plane with C-C bond.

Thus, NMR Spectroscopy gives useful information about the electronic structure of PPy which provides much more detail knowledge about polymer. Moreover, it is necessary to use such sophisticated methods that can take into account the characteristics of the polymer.

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